Available online at www.sciencedirect.com
SciVerse ScienceDirect
Energy Procedia 37 (2013) 4257 – 4267
Energy Procedia

GHGT-11

An Integrative Hierarchical Monitoring Approach for Detecting and Characterizing CO_2 Releases

U. Sauer[1*], C. Schütze[1], C. Leven[2], S. Schlömer[3], P. Dietrich[1]

[1] *UFZ – Helmholtz Centre for Environmental Research, Department Monitoring and Exploration Technologies, Permoserstrasse 15, 04318 Leipzig, Germany*

[2] *University of Tübingen, Center for Applied Geoscience Hydrogeology, Sigwartstr. 10, 72076 Tübingen, Germany*

[3] *Federal Institute for Geosciences and Natural Resources (BGR), Department 1.5 Resource Geochemistry, Stilleweg 2, 30655 Hannover, Germany*

Abstract

An integrative hierarchical monitoring approach is proposed, with the aim of reliably detecting and assessing possible leakages from storage formations into the shallow subsurface. This hierarchical approach - with method developments and applications ranging from remote sensing (infrared spectroscopy, micrometeorology-based flux measurement), to regional measurements (geophysics and chamber based soil CO_2 flux measurement), to local in-situ measurements (Direct Push Technology) - will allow large spatial areas to be consistently covered. The paper introduces a hierarchical monitoring approach applied in the MONACO project and reveals first results from measurements taken at natural analogue sites in the Czech Republic. These results indicate that the hierarchical monitoring approach represents a multidisciplinary modular concept working in different scales and resolutions.

Keywords: CCS monitoring; hierarchical monitoring approach, natural analogue; CO_2 leakages, open path spectroscopy; FTIR spectroscopy, Eddy Covariance; geophysics; Self-Potential; gas flux; Direct-Push

1. Motivation

Carbon dioxide capture and storage technology (CCS) is considered a crucial part of worldwide efforts to limit global warming by reducing greenhouse gas emissions. CCS could help achieve a large (> 85%) reduction in CO_2 emissions from fossil fuel combustion caused during power generation, industrial processes and synthetic fuel production [1]. Therefore, it has the potential to be used as a “bridging technology”, helping to mitigate carbon dioxide (CO_2) emissions until alternative energy sources are more widely available. In the last few years, several CCS research and development projects have been

*Corresponding author. Tel.: +49-341-235-1893; fax:+49-341-235-1937.
E-mail address: uta.sauer@ufz.de.

doi:10.1016/j.egypro.2013.06.328

initiated, with some governments having even already started to commercially introduce several technologies into practice. However, there are still uncertainties related to the large-scale implementation of this emergent technology, while public perception of geological CO_2 storage in the geosphere remains generally negative, motivated in particular by perceived leakage risks. There is already an EU directive on the geological storage of CO_2 in place which sets environmental rules and liability requirements for the geological storage of CO_2, stipulating that monitoring and verification are key issues to be considered.[2]. Monitoring is required as part of the approval process for underground injection and is necessary to ensure that natural resources (such as groundwater and ecosystems) are protected and that the local population is not exposed to toxic CO_2 concentrations [3]. CCS technology incorporates three important processes: CO_2 capture; compression and transport; and storage in deep (>800 m) saline formations. Besides monitoring the first two processes, the need to detect migration and leakages from storage formations also requires the development and application of effective long term monitoring tools to detect whether any increased CO_2 concentrations are observable in the atmosphere or not, either at ground surface or sub-surface level. Therefore, the main issues for future large-scale industrial application and for broader public acceptance of CCS technology are the development and validation of appropriate technologies to monitor geological CO_2 storage sites during and after operational phases and the availability of an integrated risk assessment strategy [4].

In this paper, we will present some monitoring methods as part of an integrated hierarchical approach; explain the advantages of validating these methods at a natural analogue site with natural CO_2 degassing zones, and outline findings from our first set of validation results.

2. Studying Natural Analogues

There are two ways to provide and subsequently improve efficient techniques available for detecting and monitoring potential CO_2 degassing, firstly by injecting gaseous CO_2 into a shallow aquifer or deeper formations and secondly, performing investigations on sites where large volumes of nearly-pure CO_2 accumulates naturally and/or sites where CO_2 emanates perpetually. Today, many international CCS research programs use the second approach to assess processes associated with the geological storage of anthropogenic carbon dioxide [e.g. 28].

Natural accumulations of relatively pure CO_2 are found all over the world in a range of geological settings, particularly in sedimentary basins, intra-plate volcanic regions and in faulted areas or in quiescent volcanic structures [5]. At natural analogues, where CO_2 releases occur, local focused and diffuse degassing zones can be found that present different geological and hydrological situations in different temporal and spatial scales. These sites provide the opportunity to study processes controlling how leaks may occur, their potential impacts on near-surface ecosystems and on groundwater [6].

In our opinion, the application of monitoring tools at natural analogues is necessary to determine the limits and opportunities of such method combinations for detecting leakages at the surface and to provide data for health, safety and environmental risk assessment [4]. Several natural circumstances or situations represent expected processes at man-made CO_2 storage sites and are described in *Tab.1*.

Natural analogues are the closest approximation of leakage from CO_2 storage and studying these sites can facilitate gathering information about processes leading to CO_2 release into the atmosphere. In addition, studying these natural analogues helps further understand any mechanisms or subsurface characteristics which control CO_2 transport from deeper formations into the subsurface.

Table 1. Observable phenomena art natural analogues and expected processes at man-made sites (after [4])

Observable phenomena at natural analogues	Expected processes at geological storage sites
High CO_2 concentration and high flux rates as an indicator for CO_2 releases at preferential pathways such as small vents, mofettes and vent cores	CO_2 leakage through poor quality or aging injection wells and via abandoned boreholes.
Fluid interaction caused by increased CO_2 concentration in aquifers	CO_2 leakage to surface via aquifer outflow, acidification and fluid mobilization effects, remediation, dissolution of carbonate matrices in aquifers
Diffused degassing zones with low flux rates and moderate CO_2 concentration at geological fault zones and permeable layers	Vulnerability of cap rock due to pressure induced fractures / cracks and diffuse transport to the surface combined with partly high permeable overlying sediments
Fluid – rock interaction along active fault zones as preferential pathways	Long-term alteration effects, inability of cap rock to prevent upward migration due to fracturing and faulting possibly caused by over pressuring
Vegetation anomalies due to CO_2 migration and release into upper soil horizons and lower atmosphere layers	Ecosystem vitality, influence on vegetation (indicator plants, vitality), microorganisms, animals and human beings

3. MONACO Approach

Developing and ensuring the maximum effectiveness of suitable existing and novel large scale monitoring tools is a key issue in many R&D activities associated with CCS monitoring.

Within the framework of the MONACO project (MONACO=Monitoring approach for geological CO_2 storage sites using a hierarchical observation concept), an integrative hierarchical monitoring concept is proposed, which can reliably detect and assess leakages from storage formations in the shallow subsurface (including aquifers and unsaturated zone) and CO_2 releases into the atmosphere. The proposed hierarchical approach refers to systems that are organized in the shape of a reverse pyramid, with each investigative scale linked to that which directly precedes it. As part of this integrative hierarchical monitoring concept, several methods and technologies from different disciplines (such as chemistry, hydrogeology, and geophysics) will either be combined or used complementary to one another. The MONACO approach *(Fig. 1)* will allow large spatial areas to be consistently covered, for efficient monitoring of increases in spatial and temporal resolutions. Firstly, monitoring methods for large scale application identify areas with higher CO_2 concentration in the atmosphere. Subsequently, meso-scale methods can be employed which investigate subsurface characteristics to detect potential migration pathways at pre-determined sites. Finally, point measurements enable high resolution investigations to take place at focal points. In-situ permanent monitoring in the shallow subsurface should be carried out to quantify the extent of any leakages and their resultant effect on the surrounding area/ecosystem.

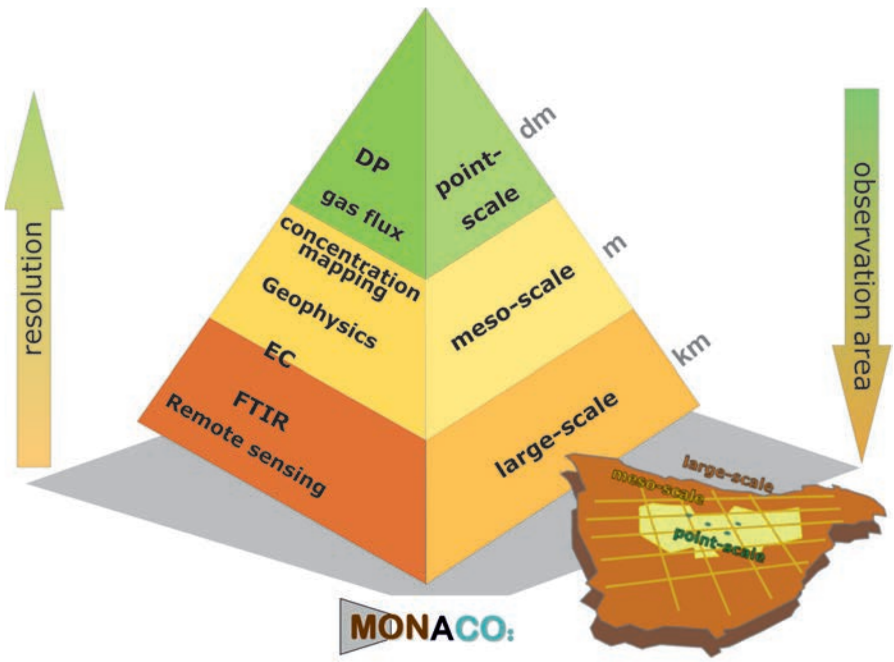

Figure 1: Hierarchical monitoring approach using different methods to monitor CO_2 leakages at different scales

1.1. Large scale atmospheric monitoring

Methods applied at a large scale can provide key information on the occurrence of CO_2 leakage and therefore help identify leakage areas for further meso-scale investigation. The impact on land surface and near-surface atmosphere caused by elevated CO_2 concentrations may alter the spectral reflectance or emissivity characteristics and can be detected using remote sensing techniques. Examples of such techniques include multi- and hyperspectral airborne remote sensing, ground-based remote infrared sensing or laser spectroscopy [8].

Within a CCS site, sensors that can measure atmospheric CO_2 anomalies over open paths hundreds of meters long present an initial impression of leakages and provide the requisite information so that further efficient observations can be made. An interesting potential concept is measuring of absorption loss due to CO_2 concentration along an open optical path [8,9].

Open-path Fourier-transform infrared (OP-FTIR) spectroscopy can be used together with onsite meteorological data to provide an ongoing assessment of quality control and to identify chemical targets in environmental applications in real time. It is a method which has already been widely developed and used [10-12].

This ground-based remote sensing method is proven to be a flexible long-path technique for the characterization of larger areas, able to simultaneously detect various volatile atmospheric compounds with a single rapid measurement. By using passive OP-FTIR spectroscopy with the ability to collect data from any direction, temporal and spatial variations in atmospheric CO_2 concentrations can be identified. However, the source processes of increased concentrations (natural CO_2 sources, anthropogenic influences, and potential storage leakages) in ambient air must be specified with further meso- and point-scale measurements. For more details please refer to another GHGT 11-paper ground based remote sensing with Open-Path Fourier-Transform Infrared (OP-FTIR) spectroscopy for large–scale monitoring of greenhouse gases by Schütze *et al.*

1.2. Meso-scale atmospheric monitoring

The Eddy Covariance (EC) method is a micrometeorological technique used to measure and determine gas fluxes in the atmospheric boundary layer (surface layer or constant flux layer) at any height above ground surface level. This technique can be applied for the determination of meso-scale CO_2 fluxes. EC is reported as being a promising tool which can be employed to monitor CO_2 leakages at CCS sites and it has been suggested it should be used in CCS monitoring programs [13-15]. In our approach, EC serves mainly as a method used to aid process understanding, helping to provide information on temporal and spatial variations at both large-and meso-scales.
EC technology utilizes highly specialized equipment which requires robust data processing and careful experiment design. For example, a tower needs to be positioned so that it exactly represents an upwind area and be situated within the constant flux area of the boundary layer. The data processing is based on a statistical procedure designed to compute turbulent fluxes of heat, water and gas exchange (e.g. CO_2, CH_4 and trace gases) between the ground surface and near-surface atmosphere, without causing any interference or damage to the ground surface. It can be used to determine an average for the integral flux of gases over larger areas and at different temporal scales [16-18].
However, this method principally depends upon different boundaries (concerning the terrain topography) and as such, it is important to keep in mind that the measured flux rates are a bulk value of all naturally occurring processes. This includes ground-level CO_2 emissions related to microbial CO_2 generation (decomposition of organic matter), plant root respiration and sinks/sources related to photosynthesis (diurnal and annual cycles, farming). Additionally, any (periodic) anthropogenic emission as well as any impact caused by meteorological or atmospheric conditions will affect the measurements. Consequently, the ability of EC technology to detect whether a release of carbon dioxide from a storage site has taken place or not strictly depends on the ratio between the integral CO_2 flux from the footprint area (baseline) and the seepage rate. A seepage rate of 0.1 t/d from a release experiment [16] was not distinguishable from background CO_2 emissions, whereas the release of 0.3 t/d significantly increased the measured flux rates compared to the base line emission rate for the observed area. Results obtained by Lewicki et al. [16] indicate that once a leakage signal is detected, EC has the potential to locate and quantify the leakage. However, simultaneous and repeated measurement of a given leakage signal by multiple EC stations with different flux source areas could improve leakage quantification. The application of EC in CCS monitoring programs should be guided by detailed site characterization, careful EC experiment design, and, ideally, the use of complementary measurement techniques [16].

1.3. Meso-scale geophysical monitoring and soil gas surveys

In a monitoring program, deep monitoring techniques (e.g. seismics) are applied to monitor the quantity and migration of CO_2 within a reservoir and adjacent formations, and as such, help contribute to geological site characterization and deliver time-lapse imaging information for CO_2 plume migration. However, our approach focuses on measurements in the near subsurface. Surface-based CO_2 soil gas concentration measurements along with geophysical methods, such as DC geoelectrics, electromagnetic (EMI) and self-potential (SP) measurements, are applied for meso-scale mapping and monitoring of CO_2 spread in the subsurface.
Two main processes can be seen as influencing factors that cause CO_2 degassing into the atmosphere. Firstly, dissolved volatile CO_2 in the pore space has an impact on electrical resistivity due to e.g. formation of carbonic acid or mineral dissolution. Electrical Resistivity Tomography (ERT) and EMI methods are used to image the resistivity distribution of shallow structures down to a depth of 50 m [19-

20]. In this context, the determination of resistivity anomalies is considered to be useful when investigating disturbances caused by variations in lithological parameters and fluid content [21-23].

Secondly, fluid movements through porous media lead to the occurrence of different effects, such as electrokinetic effects and electrochemical potential differences. Such kinds of electrokinetic effects are measured at e.g. hydrothermal systems and volcanoes [e.g.24,25]. Byrdina *et al.* [26] showed that measured SP and ERT results are related to permeable fracture zones serving as preferential pathways for soil gases and water.

The presence of flow and concentration gradients, dissolution effects of volatile CO_2 in groundwater and movements of fluids (CO_2 and H_2O) influence the measured potential differences. Thus, the proposed methods can be used for characterizing fluid flow and transport processes in permeable geological structures and also yields important information on hydraulic properties.

In addition to atmospheric gases, subsurface gases may need to be monitored to consider microbial signal, [3]. Soil-gas surveys are used for the delineation of fault zones and for the characterization of migration process dynamics. Environmental research in geothermal and volcanic areas is used to determine flux rates, which we in turn use to record reliable soil CO_2 degassing rates [27-29] either at the surface or in shallow soil depths.

Soil gas concentration and flux measurement techniques are relatively simple to perform and are valuable methods for monitoring CO_2 seepage along preferential pathways [e.g.30,31]. Long term soil gas measurements at undisturbed locations often show a strong correlation between soil-gas concentrations or fluxes and soil moisture conditions, as well as links to the meteorological situation. Therefore, it should be noted that the analysis of soil-gas concentration and flux data without taking additional external boundary conditions into account is unwise and can lead to misinterpretation.

1.4. Point Scale measurements with Direct Push

High resolution spatial and temporal monitoring of CO_2 leakages requires reliable measurements decoupled from the influence of surface processes. These measurements should be taken as close as possible to the source of the potential leakage. To investigate CO_2 fluxes in the shallow subsurface, it is imperative to perform *in-situ* measurements of CO_2 concentrations, soil permeability and to determine the lithological setting using minimally invasive drilling methods. In this regard, minimally invasive Direct Push Technology (DP), which includes methods or tools used for subsurface investigation by e.g. driving and pushing small diameter steel rods into the ground equipped with sampling tools or probes, can be said to be an ideal way of achieving this aim [32,33]. DP also allows *in-situ* measurement of physical and chemical parameters, as well as the installation of monitoring sensors into depths of up to 20 m with the least possible disturbance to the subsurface[34,35]. Furthermore, due to its flexibility and efficiency, a large number of investigations and installation points can be achieved in a short time. DP is used to investigate the spatial distribution of gas permeability and perform *in-situ* monitoring of the spatial and temporal dynamics of CO_2 concentration and fluxes. Permanent *in-situ* installations enable long-term monitoring. Additionally, isotopic composition analysis can be achieved using gas or water samples, thereby helping to identify CO_2 sources. The concept of *in-situ* measurement of CO_2 fluxes using Direct Push Technology has been successfully applied for the detection of increased radon and CO_2 fluxes at geological fault zones [36]. However, due to its invasive nature, the application of DP technology may be limited as it compromises the physical integrity of the subsurface, e.g. in the direct vicinity of CO_2 injection sites.

4. Joint interpretation

It may be difficult to distinguish between observable CO_2 fluxes originating from leakages in storage formations and background CO_2 fluxes. With the help of FTIR and EC methods, patterns of atmospheric

CO_2 distribution can be observed. Within zones of increased CO_2 concentration, the source processes (man-made, natural) need to be clarified. To achieve this, the subsurface should be monitored in detail, using geophysical methods such as ERT, SP and EMI. Subsequently, the resulting geophysical images which are generated can then be used for selecting suitable profiles for gas flux and concentration measurements. Surface-based measurements of soil CO_2 will help provide more reliable insights, in order to constrain the extent of leakages and to understand the controlling features of the observable fluid flow patterns [36]. Hence, the distribution of geophysical indicators in conjunction with observed characteristic CO_2 concentration and flux patterns is considered useful for identifying particularly important locations. At these locations, detailed investigations with DP can be performed, with the highest temporal and spatial resolution possible (as part of the subsequent level within the framework of the MONACO monitoring concept).

Gas concentration mapping and Direct Push (DP)-based soil-gas sampling is necessary to interpret the permeability of subsurface structures and to examine the spatial and temporal dynamics of CO_2 concentration and fluxes. Consequently, joint data interpretation leads to more reliable models of the investigated structures and processes associated with CO_2 migration and release.

5. Example of validation

Within the scope of this project, the hierarchical concept is tested at naturally-occurring CO_2 release sites in the Czech Republic. The Cheb Basin (NW Bohemia, Czech Republic) is a representative example of a CO_2 leaking natural analogue and offers a perfect location for directly investigating processes along preferential migration paths and for the verification of monitoring tools. Several active tectonic faults and deep processes are responsible for the occurrence of CO_2 in the Cheb Basin, where gas (up to 99.99% CO_2) is ascending via tectonic fault zones directly from the upper mantle to the surface [37]. In this investigation area, both focused small-scale CO_2 degassing sites and larger areas with diffuse degassing behavior are present, providing optimal conditions for evaluating our hierarchical concept (*Fig. 2*).

Using passive OP-FTIR spectroscopy, it was possible to identify zones with higher CO_2 concentration in the atmosphere. These were localized and selected for a detailed investigation. The images generated from our spectral measurements clearly show surface seepage of CO_2 from the soil into the atmosphere (*Fig. 3a*). The Eddy Covariance method is not applicable due to terrain topography and vegetation coverage. Furthermore, CO_2 concentration, CO_2 flux and SP mapping measurements were performed. At zones where higher CO_2 concentrations (60-90%, in a depth of 50 cm) are detectable, SP minima were found (*Fig. 3b/c*). The SP measurements show a strong correlation between CO_2 degassing zones and SP anomalies.

In addition, a geoelectric survey was carried out to provide an image of internal near surface structures to a depth of about 10m (*Fig. 3d*). The ERT results show that site-specific near surface geological features seem to exert great influence upon the degassing pattern. At zones where CO_2 concentration maxima and SP minima (at ground surface level) are detectable, a distinct subsurface resistivity anomaly pattern can be observed, extending from depths in the range 22- 36 m.

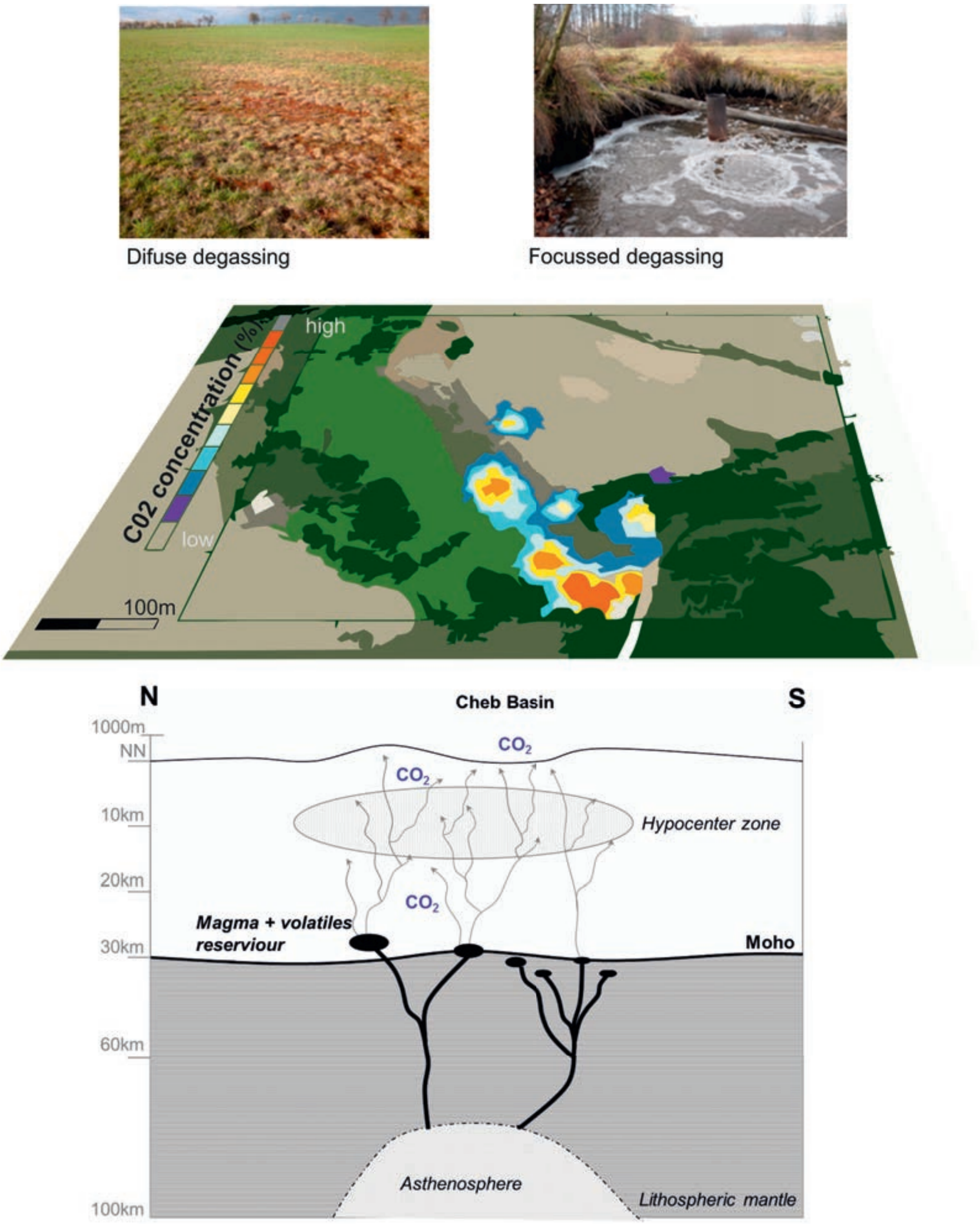

Figure 2: (a) Deep processes are responsible for the occurrence of CO_2 in the Cheb Basin (simplified according to [38]. The gas ascents along tectonic faults into near surface regions and releases into the atmosphere. At ground surface soil gas anomalies are observable by mapping the CO_2 concentration in shallow soil horizons (b) or due to apparent effects at ground surface. Both areas with focused (c) and diffused (d) degassing behavior are observable. Focused degassing is characterized by small-scale vents temporarily filled with meteoric water. At these vents high degassing rates and nearly 100% CO2 soil gas concentration at ground level are predominantly. Diffused emission is often not obvious, however sometimes distinct vegetation anomalies or indicator plants can be found.

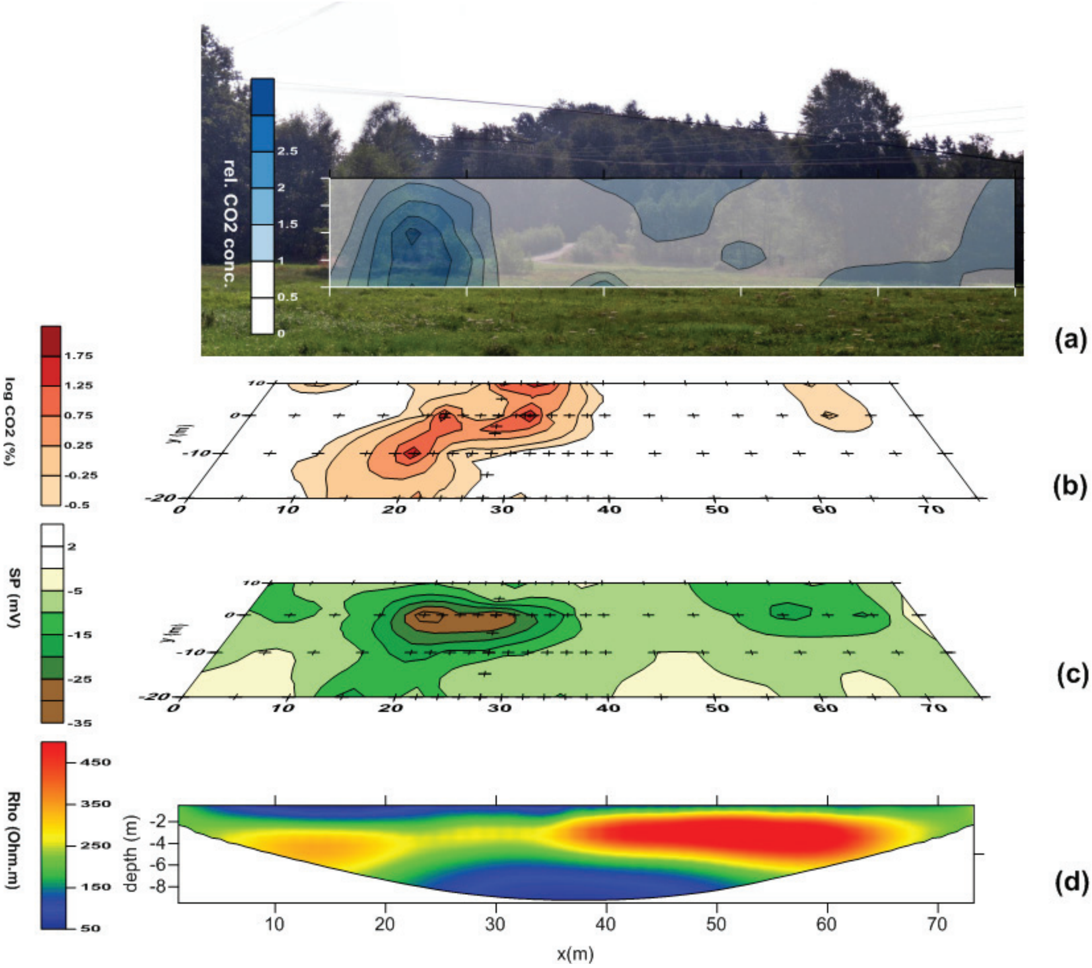

Figure 3 Results of method validation at the natural analogue; a) OP-FTIR spectroscopy scanning image localized zones with higher atmospheric CO_2 concentration , b) soil gas concentration distribution, c) negative SP anomaly correlates with higher CO_2 concentration in the atmosphere and subsurface; d)in the ERT results a distinct anomaly in the resistivity pattern is obvious.

6. Conclusion

- Natural CO_2 deposits represent unique natural analogues for evaluating and validating methods usable for the detection and monitoring of CO_2 migration in the shallow subsurface and seepage into the atmosphere. Natural analogues are characterized by optimal conditions up to critical values to evaluate and validate various monitoring methods. Furthermore, studying natural analogues can facilitate the attainment of valuable information that helps not only improve our understanding of the chemical and physical processes taking place but also provide reliable insights into processes related to CO_2 migration, trapping and leakage at CCS sites.
- The integrative hierarchical monitoring approach based on different levels of coverage and resolution is proposed to reliably detect CO_2 degassing areas and to assess CO_2 leakages from storage formations into the shallow subsurface as well as CO_2 releases into the atmosphere. The combination of large- to point-scale investigations provides the opportunity to efficiently gather information about

the site with rapid effort. Furthermore, it enables a more reliable validation of risk zones using data measured by various methods through a joint interpretation approach.

- The MONACO approach comprises the application of reliable monitoring methods from different disciplines to investigate large scales in an efficient way. The methods include OP-FTIR spectroscopy, geophysics, soil gas analytics and Direct Push technology. The proposed combination is a suitable concept for investigating CO_2 release sites including the option of modularity. Hence, the MONACO approach is expandable with other methods in all scales of coverage at any time (e.g. remote sensing or methods to determine plant stress).
- First promising results achieved from measurements taken at natural analogue sites in the Czech Republic indicate that the hierarchical monitoring approach represents a successfully multidisciplinary modular concept. The application of OP-FTIR spectroscopy in combination with soil gas surveys and geoelectrical investigations have been proven to be a valuable tool for the comprehensive characterization including the atmospheric and near surface CO_2 distribution as well as structural subsurface features

Acknowledgement

The presented work has been funded by the German Federal Ministry of Education and Research (BMBF) in the frame of the GEOTECHNOLOGIEN Program and the financial support for the projects MONACO (grant ID: 03G0785A) is gratefully acknowledged. Finally, we cordially thank our native speaker Christopher Higgins for proofreading the manuscript.

7. References

[1] International Energy Agency (IEA). CO_2 Capture & Storage. ETE01, December 2006

[2] European Parlament and the Concil, DIRECTIVE 2009/31/EC OF THE EUROPEAN PARLIAMENT AND OF THE Parliament and Council Directives 2000/60/EC, 2001/80/EC, 2004/35/EC, 2006/12/EC, 2008/1/EC and Regulation (EC) No 1013/2006, 2009

[3] NETL, Monitoring, Verification, and Accounting of CO_2 Stored in Deep Geologic Formations, United States National Energy Technology Laboratory , 2009

[4] Schütze C, Sauer U, Beyer K, Lamert H, Bräuer K, Strauch G, Felchsig Ch, Kämpf H and Dietrich P, Natural analogues – a potential approach for developing reliable monitoring methods to understand subsurface CO_2 migration processes. *Environ. Earth Sci*. **2012**, 2012, DOI: 10.1007/s12665-012-1701-4.

[5] Intergovernmental Panel on Climate Change (IPCC) Carbon Dioxide Capture and Storage, Bert Metz, Ogunlade Davidson, Heleen de Coninck, Manuela Loos and Leo Meyer *Editors*, Cambridge University Press, UK. pp 431, 2.005

[6] Pearce JM What can we learn from natural analogues? In: Lombardi S et al. Editors *Advances in the Geological Storage of Carbon Dioxide*. NATO Science Series, IV. *Earth and Environmental Sciences*, **65**, 2006: 129-140, Springer, Dordrecht, The Netherlands.

[7] Pfanz H., Vodnik D, Wittmann C, Aschan G, Batic F, Turk B, Macek I Photosynthetic performance (CO_2-compensation point, carboxylation efficiency, and net photosynthesis) of timothy grass (Phleum pratense L.) is affected by elevated carbon dioxide in post-volcanic mofette areas. *J. Environ. Exp*. Bot. **61,** 2007: 41–48.

[8] Shuler P and Tang Y, Atmospheric CO2 monitoring systems. In: Benson SM et al. Carbon Dioxide Capture for Storage in Deep Geologic Formations – Results from the CO2 Capture Project Geologic Storage of Carbon Dioxide with Monitoring and Verification. 2007; **Vol. 2,** : 1015-1030.

[9] Seto CJ and McRae GJ Reducing Risk in Basin Scale CO2 Sequestration: A Framework for Integrated Monitoring Design. *Environ. Sci. Technol*. 2011; **45**: 845–859.

[10] Harig R, Matz G and Toxis, Cloud scanning by infrared spectrometry: A scanning FTIR system for identification and visualization. *Field Analytical Chemistry and Technology* 2001**; 5 (1-2),** 75 – 90.

[11] Marshall TL, Chaffin CT, Hammaker RM and Fately WG. An introduction to open-path FT-IR Atmospheric monitoring. *Environ.Sci.Technol.* 1994; **28 (5),** 224A-232A

[12] Bradley KS, Brooks KB, Hubbard LK, Popp PJ and Stedman DH. Motor vehicle fleet emissions by OP-. FTIR, *Environ. Sci. Technol.* 2000; **34(5),** 897-899.

[13] Leuning R, Etheridge D., Luhar A and Dunse B, Atmospheric monitoring and verification technologies for CO_2 geosequestration. *International Journal of Greenhouse Gas Control*, **2(3),** 401-414, 2008.

[14] Lewicki JL, Hilley GE, Fischer ML, Pana L; Oldenburg CM; Dobeck L; Sprangler L.,Detection of CO2 leakage by eddy covariance during the ZERT project's CO2 release experiments. *Energy Procedia*, 2009; **1**, 2301-2306.

[15] Miles N, Davis K and Wyngaard J, Detecting leaks from CO2 reservoirs using micrometeo-rological methods. In: Carbon Dioxide Capture for Storage in Deep Geologic Formations-Results From the CO2 Capture Project (ed. Benson SM):1031–1044, 2005, Elsevier Sci., London, UK.
[16] Oldenburg CM, Lewicki JL and Hepple RP, Near-surface monitoring strategies for geologic carbon dioxide storage verification, Lawrence Berkeley National Laboratory Report No. LBNL-54089, 2003,Berkeley, CA, USA.
[17] Baldocchi, D., Falge, E., Gu, L. et al. FLUXNET: A new tool to study the temporal and spatial variability of eco-system scale carbon dioxide, water vapour, and energy flux densities. *American Meteorological Society*, **82**, 2001:2435-2455
[18] Smeets, CJ.PP, Holzinger, R, Vigano I, Goldstein A. H. and Röckmann T, Eddy covariance methane measurements at a Ponderosa pine plantation in California. *Atmospheric Chemistry and Physics*, **9**, 2009: 8365-8375.
[19] Rein A, Hoffmann R and Dietrich P , Influence of natural time dependent variations of electrical conductivity on DC resistivity measurements. *J Hydrol* **285(1–4)** 2004:215–232.
[20] Lamert H., Geistlinger H., Werban U., Schütze C., Peter A., Hornbruch G., Pohlert M., Kalia S., Beyer M., Schulz A., Dahmke A. and Dietrich P. Feasibility of geoelectrical monitoring and multiphase modeling for process understanding of gaseous CO2 injection into a shallow aquifer, *Environ Earth Sci* 2012. DOI: 10.1007/s12665-012-1669-0.
[21] Ball L, Ge S, Caine J, Revil A and Jardani A. Constraining faultzone hydrogeology through integrated hydrological and geoelectrical analysis. *Hydrogeol **J*** **18**, 2010: 1057–1067. DOI: 10.1007/s10040-010-0587-z.
[22] Flechsig Ch, Bussert R, Rechner J, Schütze C and Kämpf H, The Hartousov mofette field in the Cheb Basin, Western Eger Rift (Czech Republic): a comparative geoelectric, sedimentologic and soil gas study of a magmatic diffuse CO2-degassing structure. *Z Geol Wiss* **36**,2008: 177–193.
[23] Nguyen F, Garambois S, Chardon D, Hermitte D, Bellier O and Jongmans O., Subsurface electrical imaging of anisotropic formations affected by a slow active reverse fault, Provence, France. *J. Appl. Geophys*. **62**, 2007:338–355. DOI: 10.1016/j.jappgeo.2007.03.003.
[24] Revil A, Finizola A, Ricci T, Delcher E, Peltier A, Barde-Cabusson S, Avard G, Bailly T, Bennati L, Byrdina S, Colonge J, Di Gangi F, Douillet G, Lupi M, Letort J and Tsang Hin Sun E, Hydrogeology of Stromboli volcano, Aeolian Islands (Italy) from the interpretation of resistivity tomograms, self-potential, soil temperature and soil CO2 concentration measurements. *Geophysical Journal International* **186**, 2011:1078–1094. DOI: 10.1111/j.1365-246X.2011.05112.x.
[25] Lenat JF, Retrieving self-potential anomalies in a complex volcanic environment: an SP/elevation gradient approach, *Near Surface Geophysics*, 2007:161-170, DOI: 10.3997/1873-0604.2006028.
[26] Byrdina S, Revil A, Pant SR, Koirala BP, Shrestha PL, Tiwari DR, Gautam UP, Shrestha K, Sapkota SN, Contraires S and Perrier F, Dipolar self-potential anomaly associated with carbon dioxide and radon flux at Syabru-Bensi hot springs in central Nepal. *J. Geophys. Res. Solid Earth* **114**, 2009, B10101. DOI:10.1029/2008JB006154.
[27] Johansson S, Rosqvist H, Svensson M, Dahlin T, Leroux V, An alternative methodology for the analysis of electrical resistivity data from a soil gas study. *Geophys J Int* **186**, 2011:632–640. DOI: 10.1111/j.1365-246X.2011.05080.x.
[28] Carapezza ML, Ricci T, Ranaldi M and Tarchini L, Active degassing structures of Stromboli and variations in diffuse CO2 output related to the volcanic activity. *J Volcanol Geoth Res* **182**, 2009:231–245. DOI: 10.1016/j.jvolgeores.2008.08.006.
[29] Chiodini G, Cioni R, Guidi M, Marini L, Raco B, Soil CO2 flux measurements in volcanic and geothermal areas. *Appl Geochem* **13**, 1998: 543–552. DOI: 10.1016/S0883-2927(97)00076-0.
[30] Bennati L, Finizola A, Walker JA, Lopez DL, Higuera-Diaz IC, Schütze C, Barahona F, Cartagena R, Conde V, Funes R and Rios C, Fluid circulation in a complex volcano-tectonic setting, inferred from self-potential and soil CO2 flux surveys: The Santa María-Cerro Quemado-Zunil volcanoes and Xela caldera (Northwestern Guatemala). *Journal of Volcanology and Geothermal Research* **199 (3-4**), 2011: 216-229. DOI: 10.1016/j.jvolgeores.2010.11.008.
[31] Voltattorni N, Sciarra A, Caramanna G, Cinti D, Pizzino L and Quattrocchi F, Gas geochemistry of natural analogues for the studies of geological CO2 sequestration. *Appl Geochem* **24**, 2009: 1339–1346. DOI: 10.1016/j.apgeochem.2009.04.026.
[32] Leven C, Weiss H, Vienken V and Dietrich P, Direct Push technologies-an efficient investigation method for subsurface characterization." *Grundwasser* **16(4),** 2011: 221-234.
[33] Zschornack L. and Leven C, Introduction to Direct Push Technologies. Model-driven Soil Probing, Site Assessment and Evaluation - Guidance on Technologies. In M. Kästner et al. 2012, Rome, La Sapienza Publishing House, University of Rome, Italy.
[34] Hoffmann S, Beilecke T, Werban U et al. Joint application of shear wave seismics and direct push methods in the site investigation of an urban aquifer, *Grundwasser* **13(2),** 2008: 78-90.
[35] Lessoff SC., Schneidewind U, Leven C et al. Spatial characterization of the hydraulic conductivity using direct-push injection logging. *Water Resources Research* **46**, 2010.
[36] Schütze C, Vienken T, Werban U et al., Joint application of geophysical methods and Direct Push-soil gas surveys for the improved delineation of buried fault zones, *Journal of Applied Geophysics* **82**, 2012: 129-136.
[37] Bräuer K, Kämpf H , Koch U, Strauch G, Monthly monitoring of gas and isotope compositions in the free gas phase at degassing locations close to the Nový Kostel focal zone in the western Eger Rift¸ Czech Republic. *Chemical Geology* **290**, 2011: 163 – 176.
[38] Geissler WH, Kämpf H, Kind R et al. Seismic structure and location of a CO2 source in the upper mantle of the western Eger (Oh e) Rift, central Europe, *Tectonics* **24**: 2005, TC5001.